Inorg. Chem. **2005**, *44*, 9610–9612

Inorganic Chemistry
Communication

[M(R-dmet)$_2$] Bis(1,2-dithiolenes): a Promising New Class Intermediate between [M(dmit)$_2$] and [M(R,R′-timdt)$_2$] (M = Ni, Pd, Pt)

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Received July 27, 2005

We report the first examples of metal dithiolenes belonging to the class [M(R-dmet)$_2$] [R-dmet = formally monoreduced N-substituted thiazolidine-2,4,5-trithione; R = Et, M = Ni (**1**), Pd (**2**), Pt (**3**)]. A comparative spectroscopic, electrochemical, and density functional theory theoretical investigation indicates that [M(R-dmet)$_2$] complexes show features intermediate between those of the dithiolenes belonging to the previously reported classes [M(R,R′-timdt)$_2$] and [M(dmit)$_2$] (R,R′-timdt = formally monoreduced *N,N′*-disubstituted imidazolidine-2,4,5-trithione; dmit = 2-thioxo-1,3-dithiole-4,5-dithiolato). UV–vis–near-IR spectroscopy and cyclic voltammetry/differential pulsed voltammetry measurements performed on **1** and **3** proved that the new dithiolenes are stable as neutral, monoanionic, and bianionic species and feature a near-IR electrochromic absorption falling at about 1000 and 1250 nm for neutral and monoanionic species, respectively.

The interest of the scientific community toward metal 1,2-dithiolenes has been increasing continuously during the past decades, as a consequence of the numerous applications of these complexes in fields as diverse as nonlinear optics,[1] superconductivity,[2] laser Q-switching,[3] and biochemistry[4] and by virtue of their unusual electronic structure.[5] In fact, the high degree of π-electron delocalization, which involves both the organic framework and the metal center,[6] confers to dithiolene complexes of d^8 metal ions peculiar molecular properties, such as planarity, high thermal and photochemical stabilities, and intense vis−near-IR absorption, along with the ability to carry a molecular charge, which, depending on the nature of the central metal ion and of the dithiolene ligand, can vary reversibly between 2− and 2+, also assuming fractional values in nonintegral oxidation state (NIOS) salts. Among the very numerous types of dithiolene ligands,[7] dmit (dmit = $C_3S_5^{2-}$, 2-thioxo-1,3-dithiole-4,5-dithiolato; Chart 1)[8] has been the subject of a very large number of publications, mainly focused on the electrical properties of [M(dmit)$_2$]$^{x-}$ anionic complexes [x = 1, 2, fractional value in NIOS salts].[9] In fact, dmit is the only dithiolene ligand from which superconducting compounds have been obtained, and more than half of all dithiolene-based metal-like conductors derive from the dmit ligand.[2] During the past decade, we have reported the class of metal dithiolenes [M(R,R′-timdt)$_2$]$^{x-}$ (M = Ni, Pd, Pt; R,R′-timdt = formally monoreduced *N,N′*-disubstituted imidazolidine-2,4,5-trithione; x = 0, 1, 2; Chart 1), whose R,R′-timdt ligand differs from dmit in having *endo*cyclic NR groups instead of sulfur atoms.[10,11] The possibility of changing R and R′ extended the synthetic flexibility compared to that of dmit derivatives, allowing one to fine-tune several chemical−physical properties, such as the position of the peculiar very intense near-IR absorption, falling between 990 and 1070 nm for neutral [M(R,R′-timdt)$_2$] species.[12] [M(R,R′-timdt)$_2$]$^-$ monoanions feature near-IR absorptions strongly bathochromically shifted compared to the neutral ones, and remarkably dependent on the metal, so as to cover the spectral range between 1375 and 1745 nm.[13] The wavelength-selective

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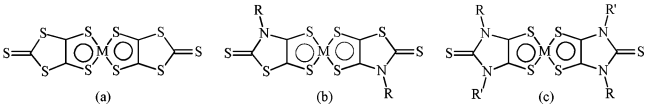
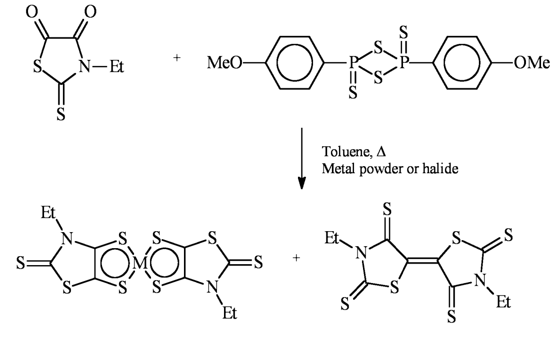
10.1021/ic051260q CCC: $30.25

Chart 1. Molecular Schemes for [M(dmit)$_2$] (a), [M(R-dmet)$_2$] (b), and [M(R,R′-timdt)$_2$] (c) Metal Dithiolenes



Scheme 1. Reaction Path in the Synthesis of [M(Et-dmet)$_2$] Dithiolenes



1-3 **4**

photoconductivity coupled to the near-IR absorption allowed for the fabrication of solid-state photodetectors operating between the first (850−1000 nm) and third (1500−1800 nm) optical-fiber windows.[13] Nevertheless, the tendency of [M(R,R′-timdt)$_2$]$^-$ anions to be oxidized to the corresponding neutral species motivated us to synthesize dithiolenes whose electronic features would be intermediate between those of the complexes deriving from the dmit and R,R′-timdt ligands to achieve the stability of anionic species of the former dithiolene derivatives, maintaining the possibility of fine-tuning the near-IR absorption through structural modifications in the NR groups.

We report here the first examples of dithiolenes belonging to the intermediate class [M(R-dmet)$_2$]$^{x-}$ [R-dmet = formally monoreduced N-substituted thiazolidine-2,4,5-trithione; R = Et, M = Ni (**1**), Pd (**2**), Pt (**3**); for **1** and **3**, $x = 0, 1, 2$; for **2**, $x = 0$; Chart 1]. The neutral complexes were synthesized in low yields by sulfuration of ethyl-2-thioxothiazolidine-4,5-dione with Lawesson's reagent[14] in the presence of the metal, as a powder in the case of nickel and as chloride in the case of palladium and platinum (Scheme 1). While **1** and **3** were isolated in their neutral state as powders very stable to air, light, and moisture, so far **2** was identified by its near-IR absorption in the reaction mixture. From the reaction mixture of **1**, tiny needle crystals of a sulfur-rich organic product, not containing the metal, were isolated. The X-ray structure of **4** established it as (*E*)-3,3′-diethyl-5,5′-bithiazolidinylidene-2,4,2′,4′-tetrathione (Et$_2$btiaz; Figure 1).[15,16] The formation of compound **4** through the coupling of two thiazolidine rings with the formation of a C═C double bond might be attributed to the instability of the thiazolidine-2,4,5-trithione ring.[17] The electrochemical properties of **1** and **3** were investigated using cyclic voltammetry (CV) and differential pulsed voltammetry (DPV; Figure 2). Two DPV-tested monoelectronic reversible processes are present for the two complexes, leading to mono- and bireduced species, respectively. The $E_{1/2}$ values, referring to the Fc$^+$/Fc couple, recorded for **1** [$E^{I}_{1/2} = -0.280(2)$ V; $E^{II}_{1/2} = -0.814(3)$ V] are just intermediate between those of [Ni(Et$_2$timdt)$_2$] [$E^{I}_{1/2} = -0.602(1)$ V; $E^{II}_{1/2} = -1.046(6)$ V] and those of [Ni(dmit)$_2$] [$E^{I}_{1/2} = -0.123(5)$ V; $E^{II}_{1/2} = -0.653(3)$ V]. The $E_{1/2}$ values determined for **3** are very close to those determined for **1** [$E^{I}_{1/2} = -0.276(4)$ V; $E^{II}_{1/2} = -0.797(7)$ V; for [Pt(Et$_2$timdt)$_2$],[10] $E^{I}_{1/2} = -0.565(3)$ V and $E^{I}_{1/2} = -1.016(4)$ V], indicating a higher stability of reduced species [M(Et-dmet)$_2$]$^-$ compared to that of [M(Et$_2$timdt)$_2$]$^-$ dithiolenes.

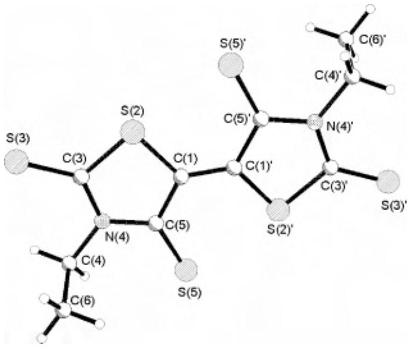


Figure 1. Perspective view and atom-labeling scheme for one of the two independent molecular units in **4**. ′ = −*x* + 1, −*y* + 1, −*z*.

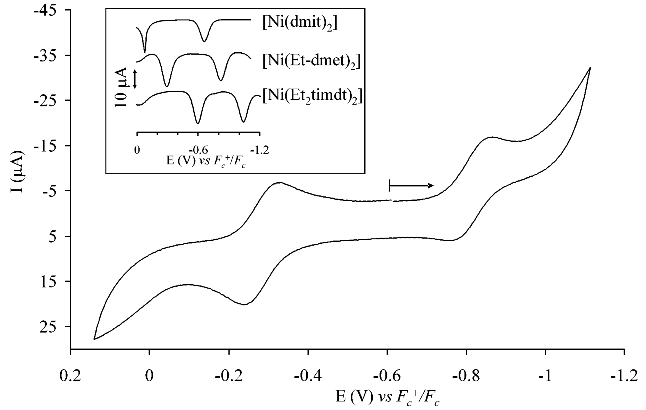


Figure 2. CV recorded at 25 °C at a platinum electrode on an anhydrous CH$_2$Cl$_2$ solution of **1**. In the inset, the DPVs of [Ni(dmit)$_2$], [Ni(Et-dmet)$_2$], and [Ni(Et$_2$timdt)$_2$] are depicted.

The characteristic near-IR transition was found for **1**−**3** beyond 1000 nm (λ_{max} = 1030, 1046, and 1010 nm in toluene, respectively; Figure 3) and very close to those

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(15) The unit cell of **4** contains two crystallographically independent centrosymmetric units (Figure S1 in the Supporting Information). A list of bond distances and angles for both units and a packing diagram in color for **4** is provided as the Supporting Information.

(16) **4** shows a high degree of π-electron delocalization, as proven by its planarity and its dark color reflecting a very unusual intense absorption in the visible region (ϵ = 11 000 M^{-1} cm^{-1} at 520 nm in toluene), largely due to a π−π* (HOMO-1)−LUMO singlet transition, calculated at 498 nm at TD-DFT level for Me$_2$btiaz. The planarity of **4** allows for the formation of stacking structures in the solid state, with *intra*molecular distances (3.6−3.8 Å) very similar to those found in the case of the [M(R$_2$timdt)$_2$] dithiolenes.

(17) In the case of the sulfuration of N,N′-disubstituted 2-thioxoimidazolidine-4,5-diones, the formation of tetrathiocino derivatives bearing two different types of C$_4$S$_4$ octaatomic rings was observed. See: Aragoni, M. C.; Arca, M.; Devillanova, F. A.; Isaia, F.; Lippolis, V.; Mancini, A.; Pala, L.; Slawin, A. M. Z.; Woollins, J. D. *Chem. Commun.* **2003**, 2226.

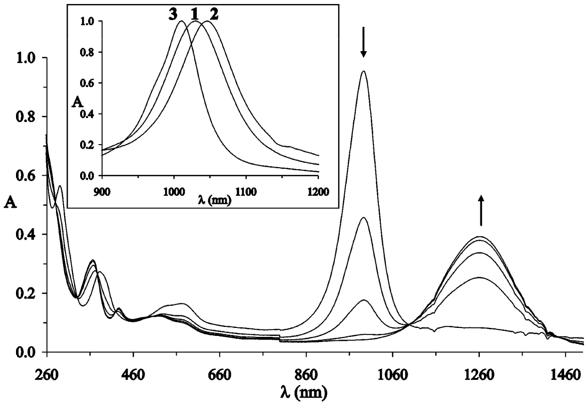

Figure 3. UV−vis−near-IR spectroelectrochemical reduction of **3** in CH_2Cl_2 at 25 °C ($C = 2.8 \times 10^{-5}$ M). In the inset, the normalized near-IR spectra recorded for **1**−**3** in toluene are shown.

recorded for neutral [M(dmit)$_2$] and [M(Et$_2$timdt)$_2$] complexes (λ_{max} = 1023 and 1003 nm, respectively, for M = Ni). Under electrochemical reduction, the position of the near-IR absorption is shifted toward lower energies in the monoreduced species (λ_{max} = 1219 and 1252 nm in CH_2Cl_2 for **1**$^-$ and **3**$^-$, respectively; Figure 3), at wavelengths between those of [M(dmit)$_2$]$^-$ and [M(R,R′-timdt)$_2$]$^-$ (λ_{max} = 1150 and 1438 nm, respectively, for M = Ni], and disappears in the bireduced species.

Despite the numerous attempts, no crystals of **1** or **3** suitable for an X-ray diffraction analysis were grown. Thus, with the aim of ascertaining the structural features of [M(Et-dmet)$_2$] dithiolenes, hybrid density functional theory (DFT)[18] calculations have been performed on the model complexes [M(Me-dmet)$_2$] [M = Ni (**5**), Pd (**6**), and Pt (**7**)], indicating that [M(R-dmet)$_2$] neutral dithiolenes should be completely planar, with the central metal ion coordinated by the two ligands in a slightly distorted square-planar coordination (Figure S3 in the Supporting Information).[19] Kohn−Sham (KS) a_u highest occupied molecular orbital (HOMO) and b_g lowest unoccupied molecular orbital (LUMO) calculated for **5**−**7** are π-type orbitals (inset in Figure S3 in the Supporting Information) involving the n p_z atomic orbitals (a.o.'s) of the four sulfur ($n = 3$) and four carbon ($n = 2$) atoms of the dithiolene system, along with the 3 p_z a.o.'s of the terminal thioketonic groups, with smaller contributions of the N(1), C(3), and S(3) *endo*cyclic atoms. Interestingly, the a.o.'s of the three metals are not involved in the HOMOs but only in the LUMOs, with contributions of n d_{xz} a.o.'s ($n = 3-5$ for **5**−**7**, respectively), increasing on passing from Ni to Pt. Time-dependent (TD)-DFT calculations assigned the near-IR transition of the neutral dithiolenes almost entirely (85.3, 82.9, and 91.8% for **5**−**7**, respectively) to a singlet HOMO−LUMO transition, with a partial ligand-to-metal charge-transfer character.[20] A diagram reporting the energies of the frontier orbitals calculated for neutral [M(dmit)$_2$] [M = Ni (**8**), Pd (**9**), and Pt (**10**)], **5**−**7**, and [M(Me$_2$timdt)$_2$] [M = Ni (**11**), Pd (**12**), and Pt (**13**)] is depicted in Figure 4. The progressive replacement of *endo*cyclic sulfurs with MeN groups is reflected by a general increase in the calculated KS eigenvalues of the corresponding orbitals. In particular, while the HOMO−LUMO energy gap is maintained approximately constant (in the range of 0.046−0.050 hartrees for M = Ni, Pt and 0.042−0.046 hartrees for M = Pd), both orbitals become progressively more antibonding and are raised in energy on passing from dmit to Me$_2$timdt. Thus, in agreement with spectroscopic data, the near-IR transition energies are calculated to remain almost unaltered, but the stability of the neutral species increases along the series, in agreement with CV/DPV measurements. In regards to the near-IR spectral features of monoreduced species, based on TD-DFT calculations performed on **5**$^-$, the low-energy transition is mainly due to a 107β−108β single occupied MO−LUMO, one-electron excitation (considering one α electron added upon reduction) and shifted to lower energies (by about 0.393 eV) compared to that calculated for **5**, in agreement with the spectroelectrochemical data.

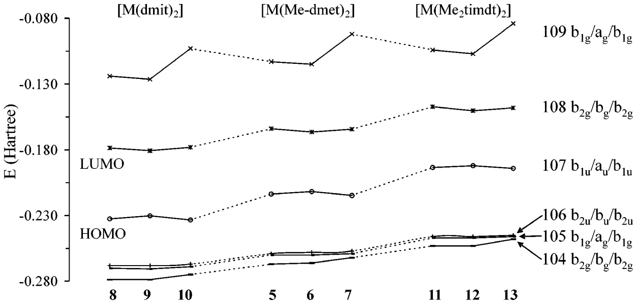

Figure 4. Calculated KS orbital energies (hartrees) of the frontier orbitals in **5**−**7**, **8**−**10**, and **11**−**13**. The labels show the representations of MOs in the C_{2h} (**5**−**7**) or D_{2h} (**8**−**13**) point groups.

In conclusion, both the experimental measurements and theoretical DFT calculations indicate **1**−**3** as the very first examples of the novel [M(R-dmet)$_2$] class of dithiolenes, whose electronic features are indeed intermediate between those of [M(dmit)$_2$] and [M(R,R′-timdt)$_2$] complexes. The energy of the electrochromic near-IR absorption of the title complexes candidate them as potential materials for near-IR−laser applications and for near-IR−photoconductivity, as was previously found for [M(R,R′-timdt)$_2$] dithiolenes. Their electrochemical properties suggest the possibility of incorporating them in NIOS salts of the type (cation)[M(R-dmet)$_2$], thus opening brand new perspectives for applications in the field of electrical conductivity of near-IR-active materials.

Supporting Information Available: Details of synthesis and characterization, crystallographic data and a CIF file for **4**, and DFT-optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) DFT calculations were performed with *Gaussian98* on model compounds **5**−**7** (C_{2h}/C_{2v}), **5**$^-$ (C_{2h}), and **8**−**13** (D_{2h}) and on Me$_2$btiaz with the mPW1PW functional. LanL2DZ basis sets with ECPs were used for the metal centers, while Schafer et al. pVDZ basis sets were used for C, H, N, and S. More details are reported in the Supporting Information.

(19) Geometry optimization was carried out on both possible isomers of **5**−**7**, which turned out to be very close in their electronic energy, with the stability of the trans form (depicted in Figure S3 in the Supporting Information for **5**) slightly increasing on passing from **5** to **7** ($\Delta E_{cis-trans}$ = 0.02, −0.05, and −0.09 kcal mol^{-1} for **5**, **6**, and **7**, respectively).

(20) Calculated excitation energies (oscillator strengths in parentheses) for the $^1A_g \rightarrow {}^1B_u$ transition: 1.429 (0.481), 1.286 (0.397), and 1.420 (0.497) eV for **5**−**7**, respectively.